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Electronic Properties of $CeNiAl_4$ Based on *ab initio* Calculations and XPS Measurements

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The $CeNiAl_4$ compound crystallizes in an orthorhombic $YNiAl_4$-type structure with a *Cmcm* space group. The earlier susceptibility data and X-ray photoelectron spectroscopy (XPS) suggested a localized character of the $4f$ states in $CeNiAl_4$ with a valence state close to a Ce^{+3} ion. In this work we present a combined theoretical and experimental study of the electronic structure for the Kondo dense system $CeNiAl_4$ based on the XPS data and *ab initio* calculations. Using the band structure calculations the theoretical XPS valence band spectra are evaluated. Below the Fermi energy the total density of states contains mainly $3d$ states of Ni hybridized with Ce $4f$ states.

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1. Introduction

Many cerium based ternary compounds of Ce-T-X-type, where T is a transition metal and X is a p-element, exhibit unusual physical phenomena such as heavy-Fermi (HF) liquid or non-Fermi-liquid (NFL) types of behavior in a metallic state or a Kondo-lattice and valence-fluctuation type of state [1]. Physical properties of this class of materials have been concerned with a variety of ground states depending on the strength of the hybridization between $4f$ electrons and conduction electrons. The different ground states such as heavy-fermion and intermediate-valence are realized due to the competition between Kondo and RKKY (Ruderman–Kittel–Kasuya–Yosida) interactions [2]. However, Ce $4f$ orbitals in the Ce-based compounds have the tendency to extend spatially over a region wider than their atomic size which gives rise to a variety of electronic effects such as delocalization, spin fluctuation, and NFL behavior [3].

$CeNiAl_4$ compound crystallize in the orthorhombic structure of the $YNiAl_4$-type, space group *Cmcm*. From magnetic susceptibility, electrical resistivity and heat capacity measurements $CeNiAl_4$ was found to be Kondo lattice system [4]. Cerium based ternary compounds demonstrate different phenomena depending on the valence of Ce ion. It is believed that the hybridization between conducting electrons and Ce $4f$ electrons should be responsible for valence state of Ce. Strong hybridization will decrease the localization of the Ce $4f$ electrons and result in non-magnetic intermediate valence behavior. On the other hand, under weak hybridization the Ce $4f$ electrons will become more localized what will lead to deep $4f$ levels. The analysis of the Ce $3d$ peaks in the framework of the Gunnarsson-Schönhammer model provides information on the localization degree. The hybridization parameter $\Delta = 2.5$ meV is found for $CeNiAl_4$ [4]. The above observations show that $CeNiAl_4$ differs significantly from the isostructural $YbNiAl_4$ compound, which is a typical fluctuating system [5].

In this paper we report the results of band structure calculations and X-ray photoelectron spectroscopy (XPS) measurements. Based on the band structure results we estimate the theoretical XPS valence band spectra.

2. Experimental and computational details

The $CeNiAl_4$ compound was prepared by induction melting of the stoichiometric amounts of the constituent elements in a water cooled boat, under an argon atmosphere.

Details of preparation are described in the Ref. [4]. The X-ray photoemission spectra were obtained with Al-K_α source using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with energy resolution of about 0.3 eV. The Fermi level $E_F = 0$ was referred to the gold $4f$-level binding energy at 84 eV. All emission spectra were measured immediately after breaking the sample in a vacuum of 10^{-10} Torr.

The spin polarized fully relativistic calculations were carried out based on the full-potential local-orbital minimum-basis scheme FPLO (FPLO-14.00-49) [6] with the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [7]. The calculations were performed for the reciprocal space mesh containing 1220 irreducible k-points from 8000 $(20 \times 20 \times 20)$ within the irreducible wedge of the Brillouin zone using the tetrahedron method for integrations [8]. The self-consistent convergence criteria were equal to 10^{-8} Ha for the total energy and for a charge density 10^{-6}. Both the volume (using constant c/a and b/a) as well as atomic positions within the *Cmcm* space group in the unit cell were optimized. The force convergence criterion was 10^{-3} eV/Å. These optimizations were performed using the scalar relativistic mode of calculations. Starting

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from the GGA we additionally tested the GGA+U approach [9] (for more details see [10]) with the Coulomb repulsion energies U varied from 0 to 6 eV and from 0 to 3 eV within the Ce $4f$ and Ni $3d$ electron shells, respectively.

In order to calculate the X-ray photoemission (PE) spectrum, the partial site contributions to the density of states in the valence band region were multiplied by the corresponding PE cross sections (tabulated in Ref. [11]) and convoluted with a Gaussian profile of 0.3 eV width, which corresponds to the experimental resolution of the hemispherical mirror analyzer

3. Results and discussion

The starting point of our calculations was to optimize the lattice constants and atomic positions within the density functional theory (DFT). We assumed constant relations of c/a and b/a taken from experimental results [12].

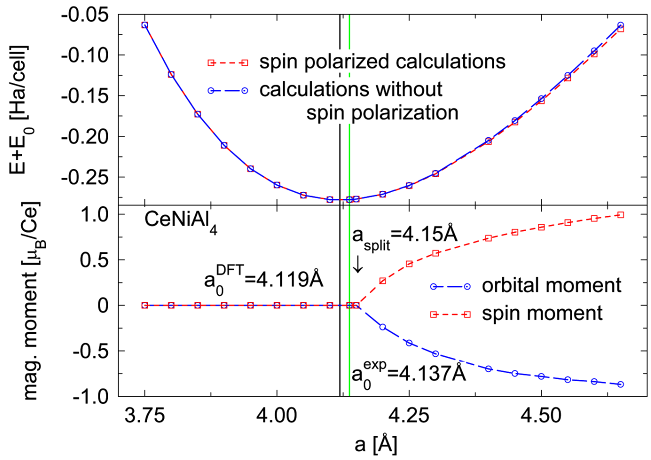

Fig. 1. Calculated total energies and magnetic moments on Ce atoms depending on lattice constant for $CeNiAl_4$.

Our calculations gave the most stable solution for $a_0^{DFT} = 4.119$ Å, which is close to the experimental value 4.137 Å and is nonmagnetic. The rest of the lattice constants have the following values: $b_0^{DFT} = 15.752$ Å and $c_0^{DFT} = 6.611$ Å. Just above $a_{split} = 4.15$ Å the ferromagnetic solutions are more stable and nonzero moments are observed, see the lower panel of the Fig 1.

For the values $(a_0^{DFT}, b_0^{DFT}, c_0^{DFT})$, the relaxed positions of atoms in the unit cell are the following: Ce(4c): (0 0.11469 $\frac{1}{4}$), Ni(4c): (0 0.77392 $\frac{1}{4}$), Al1(4b): (0 $\frac{1}{2}$ 0), Al2(4c): (0 0.92244 $\frac{1}{4}$), and Al3(8f): (0 0.31059 0.05228). These values are close to those obtained by Poduska *et al.* [12]. Presented in Figs. 2 and 3 results are obtained for the above values of the lattice constants and atomic positions.

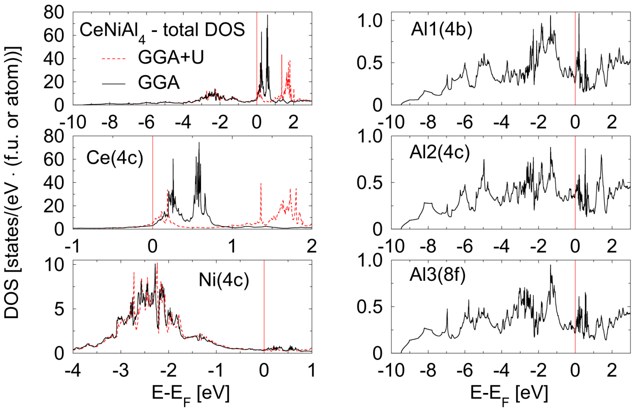

Fig. 2. Total and local DOS plots for $CeNiAl_4$: calculations performed for GGA and GGA+U, where U for Ce $4f$ electrons is equal to 6 eV and for Ni $3d$ ones is equal to 3 eV.

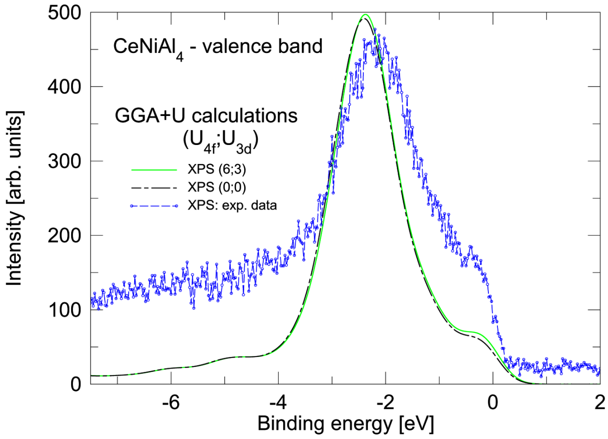

Fig. 3. V alence band region of the $CeNiAl_4$ compound obtained by XPS measurements and DFT calculations.

The total density of states (DOS) and the local contributions of the particular atoms are presented in Fig 2. for GGA and GGA+U calculations. It shows that for GGA+U case the main contribution to the DOS at the Fermi level is provided by Ce $4f$ electrons and equal to about 73% of the total value 6.7 states/(eV f.u.). The Al atoms provide about 17% and Ni one 6% (mainly $3d$ electrons). During formation of $CeNiAl_4$ compound a charge transfer takes place from cerium toward the rest of the atoms. The filled Ni $3d$ band moves to the higher binding energies, which results in low contribution of Ni to the DOS at the Fermi level. Similar situation is for the GGA calculations but the values are lower, the total DOS at the Fermi level is equal to 4.5 states/(eV f.u.). The GGA+U approach moved one of the Ce $4f$ peak toward the Fermi level and increased the DOS at the Fermi level giving the γ coefficient in the linear term of the specific heat equal to 15.9 mJ/(mol K^2). It indicates that the many body effects are very important in our case and we are not able to reproduce the experimental value of γ equal to about 0.5 J/(mol K^2) [13].

Figure 3 presents a comparison of calculated and measured photoelectron spectra. The shape of the experimental spectrum is quite well reproduced by the calculations. The main peak formed by Ni $3d$ electrons is slightly shifted toward higher binding energy. Intensity of the peak formed by Ce $4f$ electrons just below the Fermi

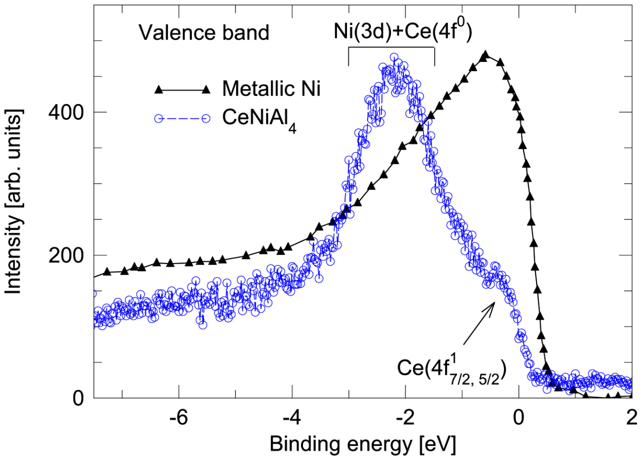

Fig. 4. Valence band region of the $CeNiAl_4$ compound measured by XPS [3]. The Ni spectrum is displayed for comparison.

level is too low. In this case one can point two reasons: the cross sections used in the calculations are for metallic monoatomic systems, not for compounds, and the peak above the Fermi level should be partially shifted towards occupied part of the valence band.

Figure 4 presents the XPS valence band of $CeNiAl_4$ in a comparison with the Ni metal. The valence band of $CeNiAl_4$ was analyzed in our previous work [4]. The valence band spectrum of pure nickel shows a main line located at –0.6 eV binding energy and the satellite at –6 eV. This suggests that there are unoccupied states in the Ni 3*d* band. The valence band of $CeNiAl_4$ is dominated by Ni 3*d* states located at about -2 eV. The contributions of the Ce 4*f* atoms are also visible, which supports additionally the statement on their localized character. We must point out that the energy position of the Ni 3*d* contribution in the XPS valence spectrum is probably considerably shifted from the Fermi level, if one compares to that of the pure Ni metal. Such a behavior may be qualitatively understood by taking into account the 3*d* band-filling effect. Fuggle *et al.* [14] studied valence band XPS of Ni-Al (Ni, Ni_3Al, NiAl, Ni_2Al_3 and $NiAl_3$) alloys. They reported that the centroid of Ni 3*d* bands shifts to higher binding energies with increasing Al content. Moreover, the absence of the –6 eV satellite in the investigated compound is another evidence of the complete filling of the 3*d*-band.

4. Conclusions

In this paper we presented a combined theoretical and experimental study of the electronic structure for the Kondo dense system $CeNiAl_4$ based on the XPS data and *ab initio* calculations. The FPLO method was used within the GGA+U formalism. The calculations reproduced well the experimental spectrum for the Coulomb repulsion energies U equal to 6 eV and 3 eV within the Ce 4*f* and Ni 3*d* electron shells, respectively. Below the Fermi energy the total density of states contains mainly 3*d* states of Ni hybridized with Ce 4*f* states.

Acknowledgments

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